SYMPOSIUM ON SYNTHETIC AND PETROLEUM-BASED LUBRICANTS
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SOME SYNERGISTIC ANTIOXIDANTS FOR SYNTHETIC LUBRICANTS

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INTRODUCTION

Oxidation stability is a major requirement for all lubricants. It is even more important for synthetic lubricants used in aircraft gas turbine engines, owing to the high oil temperature and air exposure. Two basic means are available to improve oxidation stability of synthetic lubricants: choice of base fluid and use of antioxidants. It is well known that fluids such as polyphenyl ethers are much more oxidatively stable than fluids such as dibasic acid esters. Discussions of the effect of the nature of the C-H bond on oxidation stability have been made in our previous paper [1] and by other authors such as Ingold [2] and Sniegoski [3]. However, the choice of base stock is severely limited by cost and other considerations such as volatility, flow characteristics, etc. When the choice of base fluid has been made, use of a better antioxidant is the only avenue available to improve the oxidation stability of the lubricant.

This paper describes some of the antioxidant systems which were found effective for ester type synthetic lubricants. The esters used included those based on dibasic acids, neopentyl/polyols and complex esters. The systems discussed include one or two primary antioxidants and a synergistic antioxidant. The primary antioxidant used included N-phenyl-α-naphthylamine (PANA) and p,p'-dioctyldiphenyl amine (DODPA). Synergistic antioxidants which were found to improve the effectiveness of the primary antioxidants include alkali metal compounds, aromatic diamines, heterocyclic amines, hydroxybenzophenones, and certain S &P compounds.

EXPERIMENTAL

Preparation of Alkali Metal Compounds

Alkali metal salts of partial esters of ethylenediaminetetraacetic acid (EDTA) were prepared either by partial esterification of EDTA with alcohol, followed by neutralization with Na₂CO₃ or K₂CO₃, or by the partial saponification of the tetra-ester, with NaOH or KOH [11]. The latter method gave better control and provided relatively pure products. In most cases the product used contained a mixture of the tetra-ester with the Na or K salt of the tri-ester, and possibly small amounts of salts of the di-ester. These are designated by notations such as NaBu₃ (EDTA) representing the Na salt of the tri-n-butyl ester of EDTA.

Alkali metal salts of perfluorobutyric acid and other acidic compounds were prepared by neutralization with alkali metal hydroxides, using ethanol as solvent. The neutralized product was filtered and crystallized to yield the alkali metal salt. Na acetylacetonate and Na dinonyl-naphthalene sulfonate were purchased.

Sources of Other Materials

Antioxidants such as PANA, DODPA, naphthalene diamines, hydroxybenzophenones, thioureas, and starting materials were purchased from commercial sources. Benzilidine-2, 2'-di(4-picolyl)-amine was prepared by treating 2 moles of 4-picolylamine with 1 mole of benzaldehyde.

Base Fluids

Base fluids used in testing the antioxidants were mostly commercial products. Ester A is a pentaerythritol ester of a mixture of C₅-C₁₀ fatty acids, and Ester F is a dipentaerythritol ester of similar acids. Diisooctyl azelate was purchased. Complex Ester N was prepared by esterifying 1 mole of neopentyl glycol with 2 moles of azelaic acid and 2 moles of 1-octyl alcohol. The trimethylolpropane ester of pelargonic acid was prepared by esterifying trimethylolpropane with a slight excess of pelargonic acid.

Oxygen Absorption Test

This test is a modified Dornte [4] O₂ Absorption Test and involves the bubbling of O₂ at 1 ft³/hr through 75 g of test oil held at 450°F. The volume of oxygen absorbed is monitored with a transducer and recorded automatically. The test is run until 2500 ml of O₂ (measured at 78°F and 1 atmosphere) is absorbed. The test can be run either in the presence or absence of O₂ ppm of Fe as Fe Octoate. The results of the test are reported as T₁, the induction period, and T₂, the time required to absorb 2500 ml of O₂. The induction period is the time elapsed prior to rapid change of the rate of O₂ absorption. Details of the test apparatus and procedure have been reported [5].

Oxidation - Corrosion Tests

Oxidation-Corrosion Tests are standard tests specified under MIL-L-7808 and MIL-L-9236 and Pratt and Whiting PWA521B. They generally involve the bubbling of air at 5 l/hr through 100 ml of test oil in the presence of five or six metal coupons and determining the changes in metal weight and the viscosity and acid number of the oil. Temperature and test duration vary from one version to another.

Bearing Head Test

The Bearing Head Test was conducted according to the procedures established by WADD and Pratt and Whitney. The test employs an Erdco Universal Tester equipped with a 100-mm roller bearing which rotates at a speed of 10,000 rpm under a radial load of 500 lb. Two gallons of the test lubricant is circulated through the bearing head at a rate of 600 ml/min while moist air is supplied at a rate of 9900 ml/min. Under the type of test conditions used in this paper the temperatures of the bearing and lubricant are as follows:

Type 2

Lubricant Inlet Temp., °F	400
Lubricant Sump Temp., °F	440
Bearing Temp., °F	500

The test is run with 15-hour intervals each followed by a 9-hour cooling off time until a total running time of 100 hours is accumulated. The kinematic viscosity at 210° and 100°F, TAN, pentane and benzene insolubles and ppm Fe are monitored during the test. At the end of the test the bearing head is examined and rated by both the WADD and P&W system. The filter deposit is weighed.
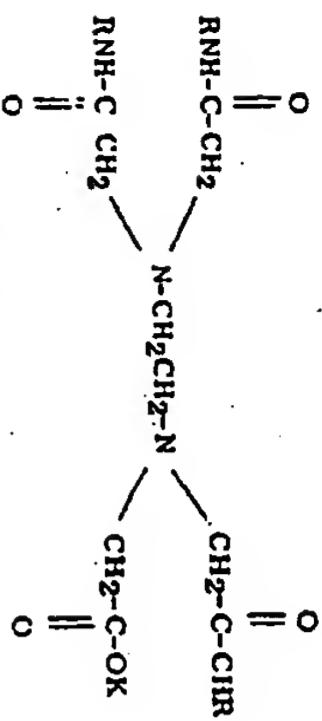
RESULTS AND DISCUSSION

Definition of Synergism and Synergist

Dolan [6] stated that the term synergism refers to the cooperative action of two or more agents in such a way that the total effect is greater than the sum of the individual effects taken independently. Emanuel [8] expressed this idea mathematically. Synergism is obtained when T₁,₂ > T₁ + T₂ where T₁ and T₂ are induction periods for each antioxidant and T₁,₂ is the induction period under the action of both. A similar mathematical definition was given by Scott [9].

The classes of compounds described below are believed to be synergists because they are poor antioxidants by themselves and when added in small concentrations to the primary antioxidant greatly increased the induction period in the Oxygen Absorption Test, significantly reduced both the viscosity and acid number increases and the metal losses in the Oxidation-Corrosion Test. Many of them also markedly improved the performance in the Bearing Head Test. Data to satisfy the mathematic definition of synergism will be shown for all but a few cases. In these cases no data were obtained to provide direct comparisons, but the fact that these synergists were poor antioxidants when used alone was well established by related data.

Alkali Metal Compounds

In 1965 and 1966 Davis and Thompson [10] reported the synergistic effect of alkali metal salts of carboxylic acids with aromatic amines in improving oxidation stability of synthetic lubricants. Using the 425°F Oxidation-Corrosion Test, they showed that Na and K stearates, when used with PANA and 5-ethyl-10, 10-diphenylphenazasiline, were outstanding among other metal stearates in reducing increases in viscosity and acid number. They used the potassium salt of the partial amide of EDTA with Primine 81R (a tertiary alkylamine of 7-14 C atoms).

RNH-C-CH₂

$$RNH-\underset{\parallel O}{C}-CH_2$$

$$N-CH_2CH_2-N$$

$$CH_2-\underset{\parallel O}{C}-CHR$$

$$CH_2-\underset{\parallel O}{C}-OK$$

Based on this synergism they formulated a MIL-L-9236B candidate lubricant which showed good results in the Oxidation-Corrosion Tests and a 525°F Bearing Head Test. However, it failed a 100-hour turbine engine test required for MIL-L-9236B lubricants, owing to excessive viscosity increase.

Our discovery of the synergism between alkali metal compounds and aromatic amines actually dated as far back as 1962. The discovery was incidental, since our objective was to develop metal deactivators based on the tetra-esters of EDTA. We found that an impure product of the tetra-n-butyl ester of EDTA containing a small quantity of Na was a strong synergistic antioxidant with PANA, while the pure ester (obtained by distillation) was not. Following this lead we prepared Na and K salts of partial esters of EDTA and other polyaminopolycarboxylic acids and tested them as synergistic antioxidants for aromatic amines.

Table I shows the type of alkali metal compounds which we found to be effective.

For the Na and K salts of partial ester of EDTA we generally used products containing the tetra-ester and the Na or K salts of partial esters. The effectiveness of these products is directly proportional to the concentration of Na or K in the product. This is shown in Figure 1 where a Ti of the required to consume 2500 ml of O₂ was plotted against the concentration of Na or K. It can also be seen that the K salts are much more effective than the Na salts. The fact that these compounds are synergistic antioxidants is indicated in Table II where O₂ Absorption Test data in the absence of Fe catalyst were shown. Thus, 1.1% PANA provided a Ti of 291 min., 1.1% NaBu₃(EDTA) provided a Ti of 99 min., but the combination of 1% PANA and 0.1% NaBu₃(EDTA) gave a Ti of 930 min. Similar conclusions of synergism can be reached by comparing Ti. Data showing the effect of Fe catalyst are shown in Table III.

By far the best alkali metal synergists we found are those derived from halogen-containing acids, especially perfluorobutyric acid. They are strong organic acids and their alkali metal salts are much more soluble in ester fluids than unsubstituted carboxylic acids. For example, a 50% solution of C₃F₇COONa remained as a clear liquid in Ester A for over one year before some crystallization took place. Among the alkali metal salts, Li ones are most soluble, followed by those of Na, K and Rb.

Data indicating synergism between C₃F₇COONa and PANA are shown in Table II. The combination of 0.1% C₃F₇COONa and 1% PANA gave a Ti of 1081 min. while each component alone gave Ti of 0 min. and 242 min., respectively. Effectiveness of alkali metal salts of other halogen-containing acids are shown in Table IV. Among the salts of C₃F₇COOH, the order of effectiveness in a finished oil containing Esters A and F (75 and 25% each) as base fluid and 1% each of PANA and DODPA as primary antioxidants, 1 mmole per kg of Li, Na and K salts gave Ti of 696, 189, and 1379 min., respectively. The Rb salt was soluble at only 0.1 mmole per kg and gave a Ti of 1471 min. at this concentration.

These alkali metal salts were not only synergistic to PANA and DODPA, but were also synergistic to other aromatic amines such as N, N'-diphenyl-p-phenylenediamine. A mixture of 1% of this amine and 0.1% C₃F₇COONa gave a Ti of 1245 min. in a base fluid consisting of a 75-25 mixture of Esters A and F in the absence of Fe catalyst. More data are shown in our patent publication (11). This synergism appears to exist in all ester fluids, including diabasic acid esters, neopentyl polyol esters and complex esters prepared from neopentylglycol, a dibasic acid and an alcohol.

Data to support this point can also be found in our patent publications (11).

The effectiveness of different alkali metal compounds is different. Table V shows a comparison of six different types of Na compounds, all of which are used at a concentration of 10-12 ppm in the presence of 1% PANA. It can be seen that the Na acetyl acetonate, NaBu₃(EDTA) and C₃F₇COONa all gave about the same Ti and Ti. On the other hand, Na dinoctylnaphthalene sulfonate was much less effective and Na lauryl phosphate, a mixture of Na salts of mono- and dilauryl acid phosphates is antagonistic toward PANA.

The effectiveness of C₃F₇COONa as a synergistic antioxidant to PANA and DODPA was also proven in the Oxidation-Corrosion Test and the Bearing Head Test. Data are shown in Table VI and in Table VII. We can see that 0.02-0.06% C₃F₇COONa substantially reduced both metal corrosion and increases in viscosity and acid number. Table VII shows that 0.06%

C₃F₇COONa greatly reduced increases in viscosity, acid number and filter deposit, while WADD and P& W cleanliness ratings were very good. Table VII also includes Bearing Head Test data which show the effect of KBu₃(EDTA) in improving all the performance characteristics. Additional bench and engine test data on a Type II synthetic lubricant containing 0.06% C₃F₇COONa as synergistic can be found in United States Patent 3,329,611 (12).

The effectiveness of these alkali metal compounds as synergistic antioxidants with aromatic amines has also been proven in a finished Type II synthetic lubricant which was commercialized after accumulating 2030 hours of successful testing in eight JT3D engines, more than 1830 hours in JT3D-3B, JT3C-12, JT8, JT-12 and TF33P7 engines and approximately 100,000 hours of flight evaluation. It was fully approved by both Pratt and Whitney and General Electric.

Aromatic and Heterocyclic Polyamines

Many aromatic diamines, including those having primary and secondary amine groups were found to be synergistic with primary antioxidants such as PANA. Table VIII shows the synergism between PANA with 1,5- and 1,8- diaminonaphthalenes and their N-alkyl derivatives. Other diamines which we found to behave similarly include o-, m- and p-phenylenediamines, 4,4'-diamino-diphenyl ether and 4,4'-diamino-diphenylmethane, etc.

The effectiveness of heterocyclic amines as synergistic antioxidants was first discovered by Eickmeyer and Ovist (13, 14). They found that compounds such as 2-amino pyridine, 3-amino-quinoline and 2,2'-dipyridylamine were synergistic with antioxidants such as PANA, phenothiazine and 8-ethyl-10, 10-diphenylphenazasiline. Subsequent work uncovered several derivatives which were more effective and more compatible with Viton rubber seals. Table IX shows the synergistic effect of these compounds with PANA in a Type I base fluid containing 20% dioctyl azelate and 80% of Complex Ester N.

Polyhydroxyphenols

Synergism between aromatic amines and phenols has been reported (16). Our search for synergistic antioxidants containing one or more phenolic hydroxy groups for use in synthetic lubricants was mostly unsuccessful. The only exception was hydroxybenzophenones containing three and four OH groups. Table X shows that, while these compounds were quite effective, other hindered phenolic compounds containing two OH groups were ineffective. A Type II synthetic lubricant containing 0.30% 2,2',4,4'-tetrahydroxybenzophenone gave a viscosity increase of 20.0% and a final acid number of 1.37 in a Type I Bearing Head Test. Details can be found in one of our patent publications (17).

Sulfur and Phosphorus Compounds

Synergism between aromatic amines and sulfur compounds is well known. During our screening program for synergistic antioxidants, we found that almost every organic sulfur compound tested acted as a synergist for aromatic amines. The problem is that most sulfur compounds contribute heavily to deposit formation, rendering them unsuitable for use in synthetic lubricants. The solution is, therefore, to find a sulfur compound which contributes least to deposits or one which is so effective that only a very small concentration is required. Table XI shows a number of such compounds and their effectiveness in improving the induction period provided by PANA. It also includes two compounds containing both S and P. Data on a few other sulfur compounds are shown in our patent publications (18,19). Since synergism between aromatic amines and sulfur compounds is known, very little effort was made to develop data to prove synergism. However, we did obtain data showing that 1% of dicresylphenylthiophosphonate gave a Ti of 10 min. and Ti of 96 min. in the test. Since 0.5 wt% PANA gave a Ti of 70 min. and the combination a Ti of 243 min., their synergistic effect is well established.

Possible Mechanism of Action

The mechanism of synergistic action of antioxidants has been reviewed and discussed by Scott (9), Emanuel (8), Ingold (7), and others (16,20). In general, the antioxidants in a synergistic mixture operate by different mechanisms of oxidation inhibition, and in so doing, re-enforce each other to such an extent that their combined-effect becomes greater than the sum of their individual effects. There are three major mechanisms of oxidation inhibition: free radical trapping, peroxide decomposition, and metal deactivation. Other mechanisms which have been proposed for synergism include regeneration of the primary antioxidant through reduction (21), formation of complexes (22,20), and inhibition of the initiation step.

For the synergistic antioxidants covered in this paper, we believe the sulfur compounds act as peroxide decomposers and the synergism is caused by the presence of both the peroxide decomposer and the aromatic amine free radical traps. The tri- and tetrahydroxybenzophenones are UV absorbers. Scott (9) indicated that UV absorbers can suppress the decomposition of

hydroperoxides into chain initiating radicals. Although synthetic lubricants operate in the relative absence of light, the energy absorbing ability of these compounds can play an important role in oxidation inhibition. It is also possible that they act as metal deactivators involving the complexing of 2 moles of the tri- or tetra-hydroxy compounds with each atom of Fe.

Synergism involving antioxidants of similar structure has been called by Scott as homo-synergism and illustrated by work of Knowton (23). He believes that amino compounds act similarly. The mechanism of homo-synergism has been attributed to regeneration of the primary antioxidant AH2 (21).

$$A + A'H_2 \rightarrow AH_2 + A'$$

Thus, although the synergistic antioxidant A'H2 is a weak antioxidant, the regeneration of the stronger antioxidant greatly increased their combined effect. Another regeneration mechanism was given by Mahoney (24) for the synergism between 2,6-di-t-butylphenol and 4-methoxyphenol. However, he showed that the rate of regeneration of the non-hindered phenol is the most important. It is believed that the aromatic diamines and heterocyclic amines discussed in this paper act in a similar manner. The regeneration mechanism also explains why a diamine is better than a mono-amine. We also believe that different amines have different reaction rates with free radicals. Some will react faster and be consumed earlier, while others react slowly but last longer. Thus, their combined use becomes more effective in trapping the free radicals. It has also been pointed out by Ingold (7) that aromatic amines also are peroxide decomposers. Therefore, synergism can take place if one of the amine antioxidants acts as a peroxide decomposer while the other acts as a free radical trap.

The least amount of literature is available to explain the synergistic effect of alkali-metal compounds. Davis and Thompson (10) suggested three possible mechanisms. First, they think that alkali metal salts direct the base oil to form oxidation products other than acid or sludge. This may be true, but it implies that they do not change the rate of oxidation. Our data on the O_2 absorption test clearly indicated that the rate of oxidation was greatly reduced. Secondly, they suggest the formation of complexes which are more potent antioxidants than the original material. We believe this is a definite possibility. Thirdly, they believe the salts may form free radicals or catalyze the antioxidants to form free radicals and interfere with autoxidation, with which we do not agree.

We believe that the mechanism of action of alkali metal salts, probably involves the formation of alkali metal cations. This is based on the fact that their effectiveness is dependent on the concentration of alkali metals (Figure 1) and that their effectiveness increases in the order of Li, Na, K and Rb. As the alkali metal atoms increase in size, the tendency to lose their outer electron and form a cation is increased. It is also supported by the fact that although the anions they are associated with have some influence, their effectiveness is not limited just to one or two types of alkali metal compounds.

There are several possible ways for the alkali metal ions to improve the effectiveness of aromatic amine antioxidants. First, the effectiveness of aromatic amines is dependent on the release of hydrogen to the free radicals. This release can be facilitated by the donation of the free electrons on the nitrogen atom to an alkali metal through coordination. Secondly, alkali metal ions can react with hydroperoxides, forming a salt which does not decompose into free radicals.

$$ROOH + Na^+ \rightarrow ROONa + H^+$$

It has also been suggested that the alkali metal compounds can probably in some way regenerate the aromatic amine or reduce its consumption and that it may inhibit the initiation step. A great deal of work is required to test these hypotheses and elucidate a viable mechanism.

Finally, it should be pointed out that the alkali metal compounds are more effective than metal deactivators. By definition, metal deactivators only cancel out, up to 100%, the catalytic effect of metals (25). Data in Table III show that 12 ppm Fe reduced T_i of 1% PANA in Ester A from 187 minutes to 60 minutes. With the addition of KBuq (EDTA) a mixture of Buq (EDTA) and KBuq (EDTA) containing 0.29% K, T_i was raised to 650 minutes, much longer than the original 187 minutes. Thus, with the data shown in Table II where substantial increases were seen in T_i in the absence of Fe, we should consider these compounds as synergistic antioxidants rather than metal deactivators.
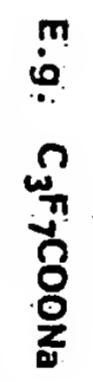

TABLE I

TYPES OF ALKALI METAL COMPOUNDS
EFFECTIVE AS SYNERGISTIC ANTIOXIDANTS

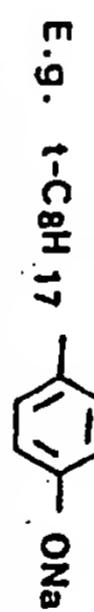1. **Alkali Metals Salts of Partial Esters of Polyaminopolycarboxylic Acids**

   E.g.

   $$BuOOC-CH_2 \diagdown N-CH_2CH_2N \diagup CH_2COONa$$
   $$BuOOCCH_2 \diagup \qquad \diagdown CH_2COOBu$$

2. **Alkali Metal Salts of Halogen-Substituted Carboxylic Acids**

   E.g. C_3F_7COONa

3. **Alkali Metal Salts of Other Carboxylic Acids**

   E.g.   Na 4-thiadodecanoate
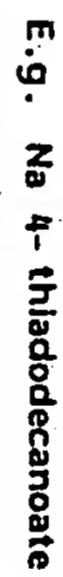
4. **Alkali Metal Salts of Phenols**

   E.g. $t\text{-}C_8H_{17}$ —⟨ ⟩— ONa

5. **Alkali Metal Salts of Sulfonic Acids**

   E.g.

   [C_9H_{19} / C_9H_{19} substituted aromatic with SO_3Na]

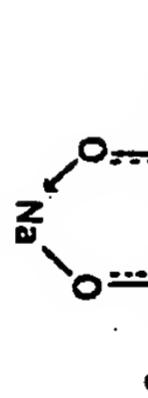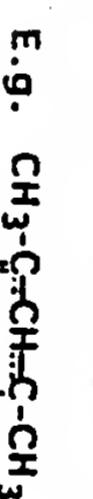6. **Alkali Metal derivatives of Enols**

   E.g.

   $$CH_3-C=CH-C-CH_3 \quad (Na)$$

TABLE II

DATA SHOWING SYNERGISM BETWEEN PANA AND ALKALI METALS COMPOUNDS

Base Fluid - Ester A, In Absence of Fe Catalyst

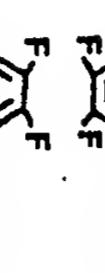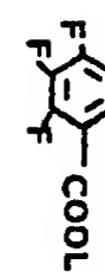| Sample	Antioxidant	Wt.%	T_i Min. (O$_2$ Absorption Test)	T_t Min.
2-1	PANA	1:1	242	291
2-2	Na Octylphenate	1:1	248	296
2-3	{ Na Octylphenate / PANA	1.0	649	691
2-4	C$_3$F$_7$COONa	1:1	none	73
2-5	{ C$_3$F$_7$COONa / PANA	0:1	1081	1115
2-6	Na 4-Thiadodecanoate	1.0	138	181
2-7	(Na 4-Thiadodecanoate	1:1	none	84
2-7	{ PANA / Na 4-Thiadodecanoate	0:1	440	487
2-8	C$_6$H$_5$N—CH$_2$CH$_2$N=CH—⟨NaO⟩]$_2$ / PANA	1.0	878	920
2-8	Na Acetylacetonate	1.0 / 0.1	none	81
2-9	{ Na Acetylacetonate / PANA	1.0	1117	1147
2-10	NaBu$_3$ (EDTA)	1.1[a]	none	99
2-11	{ NaBu$_3$ (EDTA) / PANA	0.1[a] / 1.0	896	930

• As a 10% Soln. In Bu$_4$ (EDTA)

TABLE III

EFFECT OF Fe CATALYST ON EFFECTIVENESS OF ALKALI METAL SALT OF PARTIAL ESTER AS SYNERGISTIC ANTIOXIDANTS

Sample	Base Fluid	Additives	%W	T_i Min.	T_t Min.
3-1	Ester A	PANA	1.0	187	240
3-2	Ester A	{ PANA / Fe[a]	1.0 / 0.0012	66	117
3-3	Ester A	{ PANA / K Bu$_3$ (EDTA)[b] / Fe[a]	1.0 / 1.0 / 0.0012	650	733
3-4	TMP-C$_9$[c]	PANA	1.0	138	187
3-5	TMP-C$_9$[c]	{ PANA / Fe[a]	1.0 / 0.0012	44	92
3-6	TMP-C$_9$[c]	{ PANA / K Bu$_3$ (EDTA)[b] / Fe[a]	1.0 / 1.0 / 0.0012	289	330

a. As Octoate
b. Mixt. of Bu$_4$ (EDTA) and K Bu$_3$ (EDTA), contg. 0.2978K.
c. Trimethylolpropane pelargonate

TABLE IV

EFFECTIVENESS OF ALKALI METAL SALTS OF HALOGEN-CONTAINING ACIDS

Base Formulation
Ester A   75%
Ester F   25%
PANA   +1%

Tested in absence of Fe Catalyst

Sample	Salt of Halogen-contg. Acid Formula	Wt. %	Conc. of metal ppm	O_2 Absorption Test Data T_i min.	T_t min.
4-1	None	---	---	224	266
4-2	CCl₃COONa	0.06a	65	748	768
4-3	C₃F₇COONa	0.02	18	626	661
4-4	C₇F₁₅COOLi	0.07	11.5	442	472
4-5	H(CF₂)₆COONa	0.03	19	670	700
4-6	H(CF₂)₆COOLi	0.06	20	528	550
4-7	CF₃ CF₃ (ring) COONa	0.10	64	835	882
4-8	(fluorinated ring) COONa	0.10a	13	535	577
4-9	(fluorinated ring) COOLi	0.10	37	660	698

a Incompletely soluble, filtered before test.

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TABLE V

COMPARISON OF DIFFERENT TYPES OF Na COMPOUNDS AT APPROXIMATELY SAME Na LEVEL

Basic Formulation
    Hercolube A   75%
    Hercolube F   25%
    PANA   + 1%
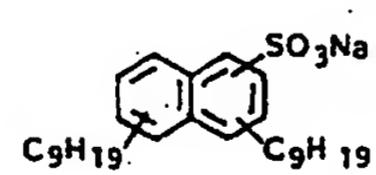   Tested in absence of Fe Catalyst

Sample	Na Compound	Concentration of Na ppm	O_2 Absorption Test T_i min.	T_t min.
5-1	None	0	224	266
5-2	Na acetylacetonate	11	594	638
5-3	Na Bu₃ (EDTA)	12	589	628
5-4	C₃F₇COONa	10	557	595
5-5	(C₉H₁₉ naphthalene SO₃Na structure)	12	295	338
5-6	Na lauryl phosphates	10	148	180

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TABLE VI

OXIDATION - CORROSION TEST DATA SHOWING EFFECT OF C_3F_7COONa

Base Formulation

Ester A	72.22
Ester F	24.08
PANA	1.00
DODPA	1.00
Bu₄ EDTA	1.50
Mono-amide of hydrogenated dimer acid	0.20
DC Fluid (200 cs;60,000MW)	0.001

Test Conditions

	400°F, 72 hrs.		425°F, 48 hrs.		450°F, 48 hrs.
C_3F_7COONa, %W	0	0.02	0	0.02	0.06
Weight Change, mg/cm²					
Cu	-1.42	-0.61	-0.93	-0.28	-0.30
Ag	+0.06	0.00	+0.03	+0.06	-0.02
Steel	-0.10	0.00	+0.03	-0.02	+0.05
Al Alloy	-0.04	+0.03	-0.02	+0.02	+0.01
Mg Alloy	-0.03	+0.05	-1.72	+0.01	-0.77
Ti	Not tested	Not tested	-0.02	+0.01	+0.04
Viscosity Increase 100°F, %	30.1	23.0	30.3	23.4	22.2
Acid No. Increase	1.82	0.57	2.21	1.06	1.27

TABLE VII

TYPE II BEARING RIG TEST DATA SHOWING EFFECT OF C_3F_7COONa AND K Bu₃EDTA

Formula

Composition, %W	A	B	C	D
Hercolube A	100	100	72.09	71.99
Hercolube F	---	---	24.21	24.25
PANA	---	+1.00	1.00	1.00
DODPA	---	+1.00	1.00	1.00
Bu₄ (EDTA)	---	---	1.50	1.50
K Bu₃ (EDTA) (0.297%K, in Bu₄ EDTA)	---	+1.00	---	---
C_3F_7COONa	---	---	0	0.06
Monoamide of Hydrogenated Dimer Acid	---	---	0.20	0.20
DC Fluid (200 cs; 60,000 MW)	---	---	+0.001	+0.001

Results

	A	B	C	D
Viscosity Increase, 100°F, %	2,190	291	271	50.0
Final Acid No.	9.98	5.65	5.69	0.93
100 mesh filter deposit, mg.	5.60	0.87	0.29	1.24
WADD Demerit Rating	128	38	53	58
P&W Rating	2,3,2	1,1,1	1,1,1	1,1,1

TABLE VIII

NAPHTHALENE DIAMINES AS SYNERGISTIC ANTIOXIDANTS

Base Fluid: Hercolube A, in presence of 12 ppm Fe

Sample	Antioxidant	%W	O$_2$ Absorption Test	
			T$_i$ min.	T$_f$ min.
8-1	PANA	1.5	62	109
8-2	1,8 diaminonaphthalene	1.5	131	181
8-3	{ PANA 1,8-diaminonaphthalene	1.0 0.5	265	308
8-4	1,5-diaminonaphthalene	1.5	150	193
8-5	{ PANA 1,5-diaminonaphthalene	1.0 0.5	257	317
8-6	N-Octyl-1,5-diaminonaphthalene	1.5	112	157
8-7	{ PANA N-Octyl-1,5-diaminonaphthalene	1.0 0.5	258	297
8-8	N-Octadecyl -1,8-diaminonaphthalene	2.0	100	142
8-9	PANA	2.0	74	126
8-10	{ PANA N-Octodecyl-1,8-diaminonaphthalene	1.0 1.0	295	335

TABLE IX

HETEROCYCLIC AMINES AS SYNERGISTIC ANTIOXIDANTS

Test in presence of 12 ppm Fe
Base Fluid: 80% Complex Ester N, 20% - Dioctyl azelate

Sample	Antioxidant	%W	O$_2$ Absorption Test Data	
			T$_i$ min.	T$_f$ min.
9-1	PANA	0.5	76	163
9-2	2- Anilinoquinoline	1.0	14	109
9-3	{ 2-Anilinoquinoline PANA	1.0 0.5	165	210
9-4	Benzilidene 2,2'- di-(4-picolyl)amine	0.2	12	81
9-5	{ Benzilidene 2,2'- di-(4-picolyl)amine PANA	0.2 0.5	168	218
9-6	{ 2,6-di(2- pyridylamino) - 4-t-octylphenol PANA	1.0 0.5	211	281

TABLE X

HYDROXYBENZOPHENONES AS SYNERGISTIC ANTIOXIDANTS

Test in presence of 12 ppm Fe

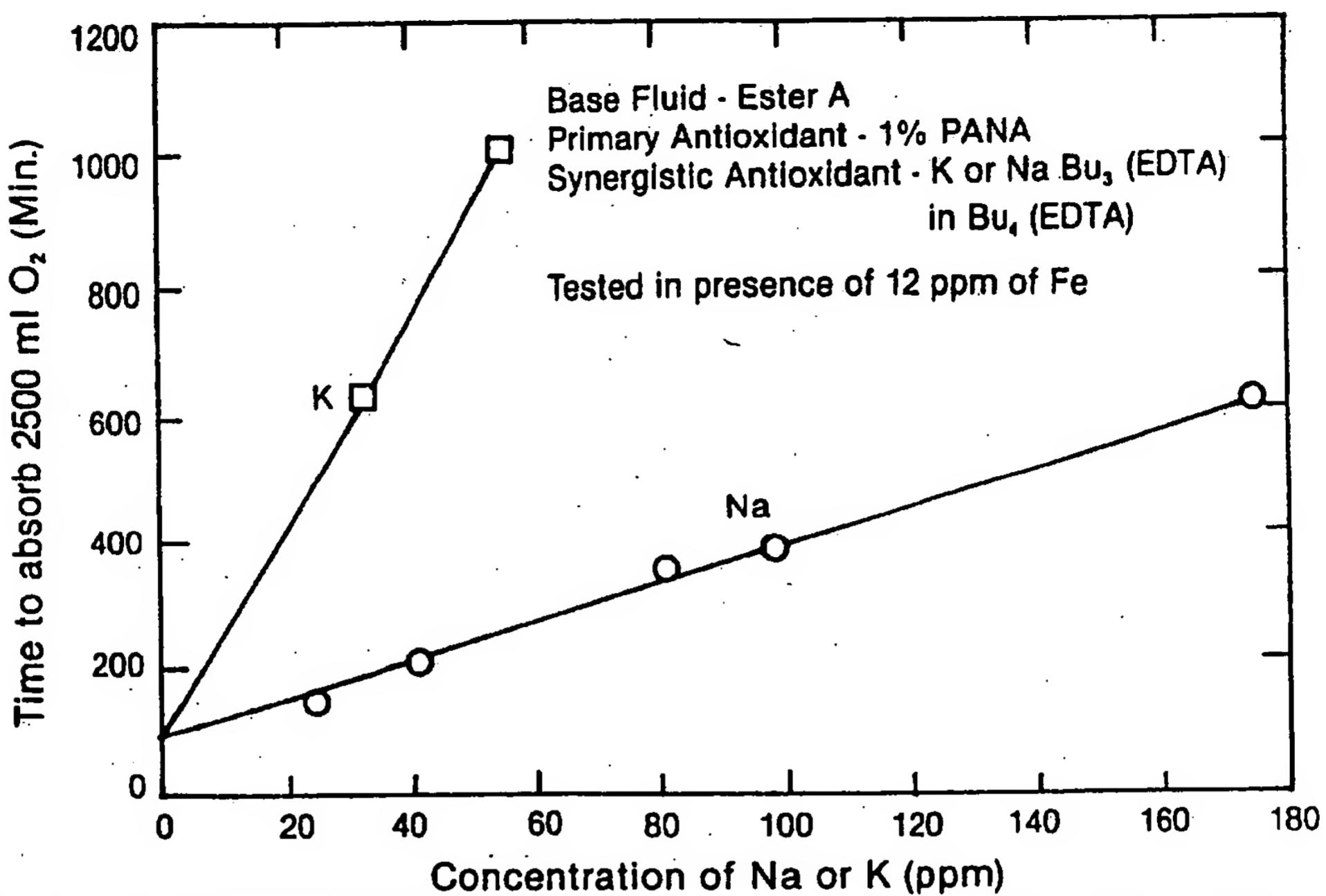| Sample	Base Fluid	Antioxidant	%W	T_i min.	T_t min.
10-1	{ Hercolube A 75% / Hercolube F 25% }	PANA / DODPA	1.0 / 1.0	46	93
10-2	{ Hercolube A 75% / Hercolube F 25% }	2,2',4,4'-tetradihydroxy-benzophenone	0.5	0	69
10-3	{ Hercolube A 75% / Hercolube F 25% }	2,2',4,4'-tetrahydroxy-benzophenone	0.5	266	304
10-4	{ Hercolube A 72.22% / Hercolube F 24.08% / Buq EDTA 1.50% / Monoamide of hydrogenated dimer acid 0.20% }	PANA / DODPA	1.0 / 1.0	23	87
10-5	{ Hercolube A 72.22% / Hercolube F 24.08% / Buq EDTA 1.50% / Monoamide of hydrogenated dimer acid 0.20% }	PANA / DODPA / 2,4,4'-trihydroxy benzophenone	1.0 / 1.0 / 0.5	238	272
10-6	{ Hercolube A 72.22% / Hercolube F 24.08% / Buq EDTA 1.50% / Monoamide of hydrogenated dimer acid 0.20% }	PANA / DODPA / 3,3',5,5'-tetra-t-Bu-4,4'-dihydroxybi-phenyl	1.0 / 1.0 / 1.0	43	86
10-7	{ Hercolube A 72.22% / Hercolube F 24.08% / Buq EDTA 1.50° / Monoamide of hydrogenated dimer acid 0.20% }	PANA / nODPA / Bis (3,5-di-t-Bu-4-hydroxy)methane	1.0 / 1.0 / 1.0	61	101

TABLE XI

EFFECTIVENESS OF SOME S & P COMPOUNDS IN IMPROVING EFFECTIVENESS OF PANA

Tested in absence of Fe catalyst
Base Fluid: 80% Complex Ester N, 20% Dioctyl Azelate
Primary Antioxidant: 0.5%W PANA

Sample	Synergistic Antioxidant	%W	T_i min.	T_t min.	V_i ml.
11-1	None	0	76	163	217
11-2	s-Diphenylthiourea	0.1	152	202	589
11-3	s-Diphenylthiourea	1.0	> 492	492	2500
11-4	N-phenyl-N'-2-pyridylthiourea	0.2	380	406	2045
11-5	s-Di-tolyl-thiourea	0.5	> 399	399	2500
11-6	4,4'-Bis(dimethylamino)-thiobenzophenone	0.1	241	275	1200
11-7	2-Thiobenzoylaminopyridine	0.5	285	349	1175
11-8	N,N'-dilaurylthioxamide	0.5	263	327	1430
11-9	2,2'-Dithio (benzothiazole)	0.2	160	235	525
11-10	O,O,O-Tributylphosphothioate	1.0	143	195	650
11-11	Dicresylphenylthiophosphonate	1.0	243	338	1140

Figure 1
Effect of Concentration of Alkali Metal on O₂ Absorption

Base Fluid - Ester A
Primary Antioxidant - 1% PANA
Synergistic Antioxidant - K or Na Bu₃ (EDTA)
in Bu₄ (EDTA)

Tested in presence of 12 ppm of Fe

designing the O_2 Absorption Test and discovery of the synergistic effects of the heterocyclic amines.

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